

Article

Research on the Mechanical Properties and Microstructure of Fly Ash, Slag, and Metakaolin Geopolymers

Zhiqiang Xing ^{1,*}, Zekang Li ¹, Peng Wang ², Zeming Song ³ and Li Wu ⁴

¹ School of Civil Engineering and Transportation, Northeast Forestry University, Harbin 150040, China; lzk4taiyang@outlook.com

² College of Engineering and Technology, Harbin Vocational College of Science and Technology, Harbin 150300, China; 15804633081@139.com

³ Heilongjiang Construction Technology Development Center Co., Ltd., Harbin 150046, China; fengmw2008@sina.com

⁴ Heilongjiang Pengcheng Inspection and Testing Co., Ltd., Harbin 150086, China; 13945064500@139.com

* Correspondence: xingzhiqiang202507@163.com; Tel.: +86-188-4677-7996

Abstract

Geopolymer materials possess several outstanding advantages, including the wide availability of raw materials, an energy-saving and environmentally friendly production process, and excellent engineering technical performance. They are regarded as a new type of green building material that can achieve high-value-added resource utilization of industrial solid waste. They are one of the current research hotspots in the field of materials. Fly ash and slag, the most common industrial wastes in China, have been discharged in large quantities, significantly impacting the country's ecological environment. Based on this, this paper primarily investigates the mechanical properties and strength formation mechanism of geopolymer paste to develop geopolymer materials with enhanced mechanical properties. This research uses metakaolin as the silicate raw material and uses sodium silicate mixed with NaOH as the alkali activator to prepare geopolymer paste. By adding fly ash and slag, the mechanical properties of the geopolymer paste are improved. The effects of the alkali activator modulus, Na₂O equivalent, and content of fly ash and slag on the setting time and strength of geopolymer paste are studied. XRD, FTIR, and SEM are employed to characterize the phase, molecular structure, and microscopic morphology of geopolymer paste, as well as to analyze the microstructure and reaction mechanism of these materials. The results show that the setting time of the geopolymer increases with the increase in modulus and shortens with the increase in Na₂O equivalent. Fly ash and slag, respectively, act as retarders and early strength promoters. The ratio of n(SiO₂)/n(Al₂O₃) (that is, the modulus of the alkali activator) of the geopolymer is an important factor affecting its strength. The metakaolin and fly ash–slag–metakaolin exhibit the best mechanical properties when their molar ratios are 2.97 and 3.26, respectively. Through microscopic characterization using XRD, FTIR, and SEM, it is observed that fly ash–slag–metakaolin exhibits the most complete polymerization reaction, generates the most amorphous silicate aluminosilicate gel, and displays the best inter-gel bonding effect, resulting in the best mechanical properties.

Keywords: industrial solid waste; geopolymer materials; mechanical properties; scanning electron microscopy



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1. Introduction

The rapid development of infrastructure projects has led to a significant increase in the demand for cement. This widespread use can be attributed to its diverse sources, low construction costs, and broad applicability across various aspects of daily life [1]. Since the invention of Portland cement, it has not only supported industrialization, but also played a crucial role in advancing the social market economy [2]. However, the production of Portland cement is associated with high energy consumption and substantial environmental impacts throughout its lifecycle. The manufacturing of one million tons of concrete results in approximately one million tons of CO₂ emissions, accounting for around 7% of global CO₂ emissions. Furthermore, the process releases significant amounts of nitrogen oxides (NO_x), sulfur oxides (SO_x), particulate matter, and other harmful pollutants into the atmosphere [3–5]. In addition, Portland cement-based materials face challenges related to durability and limitations in adopting advanced concrete technologies [6]. Consequently, the search for environmentally sustainable alternatives has become increasingly urgent, with geopolymers emerging as a promising solution to this challenge.

Geopolymer is an inorganic silicate–aluminate material exhibiting ceramic-like properties [7–10]. It is synthesized through a chemical reaction between an alkaline activator and aluminosilicate sources rich in reactive silica and alumina. At the microscopic level, geopolymer forms a novel three-dimensional cementitious network structure via the depolymerization of raw materials—such as kaolin and industrial solid wastes—under highly alkaline conditions [11–13]. A wide variety of raw materials can be utilized in its production, including natural aluminosilicate minerals, kaolin, fly ash, and other industrial by-products. The manufacturing process is energy-efficient, requiring only 1/6 to 1/4 of the energy needed for cement concrete production, approximately 1/20 that of ceramics, 1/7 that of steel, and as little as 1/150 that of plastic products. Notably, geopolymer synthesis does not emit nitrogen oxides (NO_x), sulfur oxides (SO_x), or carbon monoxide (CO), and its associated CO₂ emissions are roughly one-tenth of those produced during the manufacture of equivalent-performance Portland cement [14–16]. If geopolymer can be successfully produced using industrial and construction waste as primary raw materials to replace conventional silicate cements, it would not only contribute to effective waste management and pollution mitigation, but also reduce the demand for natural resource extraction, thereby supporting environmental sustainability [17–19].

Geopolymer can be synthesized from industrial waste materials rich in silicate-based substances (such as silica powder, fly ash, and slag) and natural minerals (such as metakaolin and zeolite) in an alkaline environment [20]. After being stimulated by the alkaline environment, the raw materials re-crystallize to form a three-dimensional, network-like cementitious material, with oxygen–silicon tetrahedra and aluminum–oxygen tetrahedra as the primary components. The chemical equation can be expressed as $Mn\{-(SiO_2)_z-AlO^{2-}\}_n$, where z represents the molar ratio of silicon to aluminum elements, and M can represent alkali metals, such as sodium and potassium ions. Geopolymer materials exhibit rigidity similar to that of cement, while also displaying the brittleness characteristic of ceramic materials, resulting in a combination of high brittleness and poor toughness [21]. The factors influencing the polymeric properties of fly ash-based geopolymers were examined by A Lăzărescu et al. [22,23]. Parameters such as the molarity of sodium hydroxide (ranging from 8 M to 12 M) and the ratio of alkaline activators (ranging from 0.5 to 2.5) were systematically analyzed to evaluate their influence on the mechanical properties of geopolymer paste. Experimental results indicate that the compressive strength of fly ash-based geopolymer paste, prepared using Romanian local raw materials, increases with a higher sodium hydroxide concentration and an increased Na₂SiO₃/NaOH solution ratio. The geopolymer reaction can be divided into the following two processes: depolymerization and polycondensation.

First, amorphous materials containing silicate-based elements are dissolved by alkaline sodium hydroxide and metal silicate solutions. The dissolved substances undergo polycondensation reactions to form amorphous polymers, which further solidify and harden [24]. Geopolymer exhibits excellent mechanical properties, high temperature resistance, and corrosion resistance, and has been applied in the aerospace industry, forging of non-ferrous metals, metallurgical industry, civil engineering, and the plastic industry abroad [25,26]. In conclusion, geopolymer can be a good alternative to cement in the construction industry.

However, a large number of studies have focused on the compressive performance of fly ash-based geopolymer, while the flexural performance has been relatively ignored. Moreover, fly ash-based geopolymer generally has low flexural strength [27,28]. Metakaolin, fly ash, and slag are rich in and prone to releasing silicon and aluminum elements required for the formation of geopolymer networks under alkaline conditions (reactivity), and, at the same time, have significant environmental and economic benefits (utilization of industrial solid waste and cost reduction). Their respective characteristics also provide flexibility for the design and optimization of geopolymer performance. Therefore, this paper optimizes the combination of metakaolin, slag powder, and fly ash, uses NaOH to adjust the water glass as the alkali activator, and improves the mechanical properties of the geopolymer gel system by changing parameters such as alkali content and water glass modulus; on this basis, microscopic experimental research is conducted on the combinations with a better mechanical performance to reveal the strength formation mechanism of geopolymer and provide technical references for the application of geopolymer.

2. Test Materials

2.1. Material Introduction

Metakaolin is a dehydrated aluminum silicate compound ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) produced through the thermal dehydration of kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) at temperatures ranging from 600 to 900 °C. Blast furnace slag is an industrial by-product generated during the production of pig iron in blast furnaces. It contains a significant proportion of amorphous silicate compounds and exhibits pozzolanic or hydraulic properties similar to those of cement. Partially replacing cement with metakaolin in concrete can effectively enhance the early strength of the concrete and reduce its production cost. Fly ash is fine ash captured from the flue gas after coal combustion, and it is the main solid waste discharged by coal-fired power plants. The main oxide composition of fly ash from China's thermal power plants is as follows: SiO_2 , Al_2O_3 , FeO, Fe_2O_3 , CaO, TiO_2 , etc. The chemical composition information of the three silicate raw materials was measured using an X-ray fluorescence spectrometer (XRF, Revontium, Harbin, China) and is presented in Tables 1–3.

Table 1. Chemical composition of metakaolin.

Chemical Composition	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2	CaO	Na_2O	MgO	Loss
Content (%)	50.14	41.11	0.76	0.55	0.24	0.17	0.06	0.06	6.91

Table 2. Chemical composition of slag.

Chemical Composition	CaO	SiO_2	Al_2O_3	MgO	SO_3	TiO_2	MnO	Fe_2O_3	K_2O	Na_2O	SrO	Loss
Content (%)	35.9	34.1	15.36	6.58	2.5	2.41	1.07	0.83	0.06	0.4	0.13	0.66

Table 3. Chemical composition of fly ash.

Chemical Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	TiO ₂	MgO	SO ₃	Na ₂ O	P ₂ O ₅	SrO	Loss
Content (%)	61.88	25.3	4.28	3.96	1.33	1.27	0.73	0.46	0.31	0.12	0.36

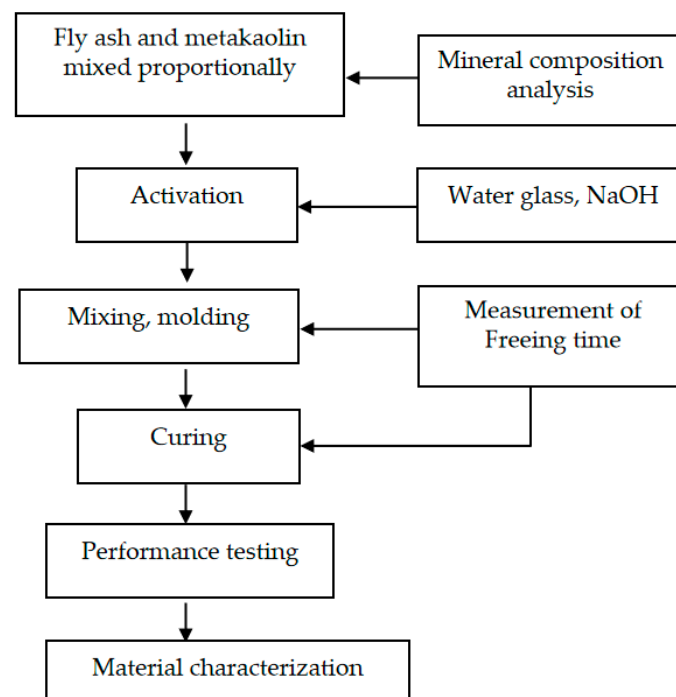
The geopolymer was prepared using sodium hydroxide and water glass as alkaline activators. The main technical parameters of water glass are shown in Table 4. Granular sodium hydroxide with a purity greater than 96% was used.

Table 4. Technical parameter of the water glass.

Technical Parameters	Na ₂ O Content (%)	SiO ₂ Content (%)	Modulus	Density (kg/m ³)	Baume Degrees
Measured value	8.5	26.5	3.1	1480	40

2.2. Mix Proportion Design and Preparation

According to the test mix ratio, we accurately weighed the raw powder materials of metakaolin, slag, and fly ash and mixed them evenly. We calculated the silicate modulus and weighed the water glass, NaOH, and water to prepare the alkali activator solution. After the alkali activator solution was cooled to room temperature, we added it to the powder raw materials and mixed in the cement clean slurry mixer for 4 min to obtain the geopolymer slurry. Standard specimens measuring 40 mm × 40 mm × 160 mm were prepared and cured in a standard curing box. After reaching the age, strength tests were conducted. The tested specimens failed and were subjected to microscopic material characterization. The specific process is shown in Figure 1.

**Figure 1.** Flowchart of geopolymer preparation.

In this paper, the mix ratio of geopolymers was designed by using the following three factors: the modulus of sodium silicate, the equivalent of basic oxides, and the water–solid ratio. First, we mixed water glass with NaOH to adjust the required modulus of water glass. Then, we determined the required silicon–aluminum raw materials through the

equivalent of alkaline oxides; finally, we determined the required water volume based on the water–solid ratio.

(1) Modulus of alkali activator

The modulus of the alkali activator refers to the molar ratio of silicon dioxide to the basic oxide in the mixed liquid of water glass and NaOH, that is, $M = n(\text{SiO}_2)/n(\text{Na}_2\text{O})$.

(2) Basic oxide equivalent

The equivalent of basic oxides refers to the mass ratio of the equivalent basic oxides (such as K_2O , Na_2O , etc.) in the alkaline activator to the mass of the silicon–aluminum raw materials being excited. In this paper, a mixed solution of water glass and NaOH is used as the activator. The equivalent of basic oxides is the mass of the equivalent NaOH in the mixed solution of the alkaline activator. The silicon–aluminum raw materials refer to the mass of metakaolin, fly ash, and slag.

(3) Water–solid ratio

The water–solid ratio refers to the mass ratio of all water in the alkaline activator solution to the silicon–alumina raw materials, which include the masses of kaolin, fly ash, and slag.

The water–solid ratio of geopolymer is set at 0.5, and the following three factors are selected: sodium silicate modulus, Na_2O equivalent, and the dosage of fly ash and slag. Based on the previous experimental observations, when the modulus of water glass is less than 0.9, all the geopolymers are instantaneously condensed. When the modulus of sodium silicate is greater than 1.5, the setting time of the geopolymer exceeds 48 h, making it difficult to apply in practical engineering. Therefore, the parameter levels of sodium silicate are 1.0, 1.2, and 1.4, and the equivalent levels of Na_2O are 10%, 12%, 14%, and 16%. The blending ratio of silicon–aluminum raw materials is as follows: 100% metakaolin, 60% metakaolin +40% fly ash, 60% metakaolin +40% slag, and 100% metakaolin +20% fly ash +20% slag. The design of the blending ratio is shown in Table 5.

Table 5. Design table of geopolymer mix proportion.

Table	$n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$	$n(\text{Na}_2\text{O})/n(\text{Al}_2\text{O}_3)$	$n(\text{H}_2\text{O})/n(\text{Al}_2\text{O}_3)$
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.0}\text{N}_{10}$	2.47	0.4	6.75
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.0}\text{N}_{12}$	2.55	0.48	6.72
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.0}\text{N}_{14}$	2.63	0.56	6.69
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.0}\text{N}_{16}$	2.71	0.64	6.66
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.2}\text{N}_{10}$	2.55	0.4	6.61
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.2}\text{N}_{12}$	2.65	0.48	6.55
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.2}\text{N}_{14}$	2.74	0.56	6.49
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.2}\text{N}_{16}$	2.84	0.64	6.43
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.4}\text{N}_{10}$	2.63	0.4	6.46
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.4}\text{N}_{12}$	2.75	0.48	6.38
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.4}\text{N}_{14}$	2.86	0.56	6.29
$\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.4}\text{N}_{16}$	2.97	0.64	6.21
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.0}\text{N}_{10}$	3.06	0.5	8.46
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.0}\text{N}_{12}$	3.16	0.6	8.42
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.0}\text{N}_{14}$	3.26	0.7	8.39
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.0}\text{N}_{16}$	3.36	0.8	8.35
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.2}\text{N}_{10}$	3.15	0.5	8.28
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.2}\text{N}_{12}$	3.28	0.6	8.21
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.2}\text{N}_{14}$	3.4	0.7	8.14
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.2}\text{N}_{16}$	3.52	0.8	8.07

Table 5. Cont.

Table	$n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$	$n(\text{Na}_2\text{O})/n(\text{Al}_2\text{O}_3)$	$n(\text{H}_2\text{O})/n(\text{Al}_2\text{O}_3)$
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.4}\text{N}_{10}$	3.26	0.5	8.1
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.4}\text{N}_{12}$	3.4	0.6	8.0
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.4}\text{N}_{14}$	3.54	0.7	7.89
$\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.4}\text{N}_{16}$	3.68	0.8	7.78

Note: P—refers to metakaolin, F—refers to fly ash, S—refers to slag, M—denotes modulus, N—represents Na_2O equivalent.

2.3. Test Programs

2.3.1. Setting Time

The timing was initiated upon the addition of the alkali activator to the powdered material. The mixture was then slowly blended in an NJ-160B cement slurry mixer (Beijing Huiju Laboratory Equipment Co., Ltd., Beijing, China) for 2 min, followed by high-speed mixing for an additional 2 min to ensure a homogeneous and flowable slurry. Afterward, the slurry was poured into the test mold and transferred to a YH-40B standard (Beijing Huiju Laboratory Equipment Co., Ltd., Beijing, China) curing chamber for curing. The setting time was subsequently determined as illustrated in Figure 2.

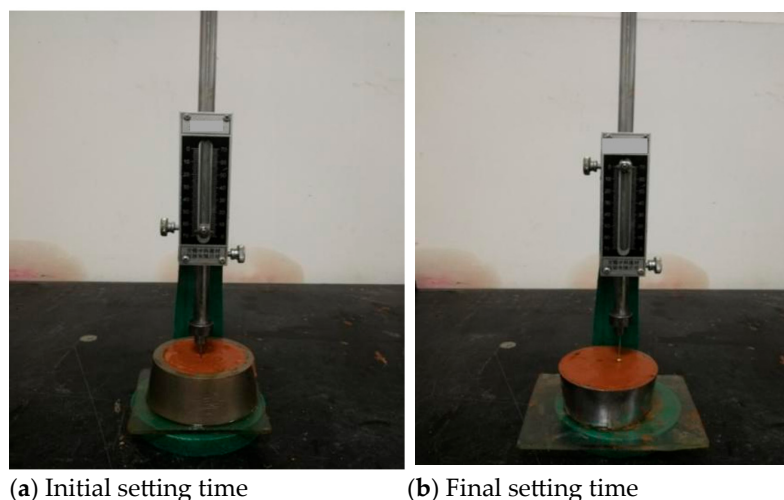


Figure 2. Setting time determination.

(1) Determination of initial setting time

Replace the Vicat apparatus with the initial setting test needle. After adding the alkali activator, keep the specimen in the curing chamber for 30 min. Then, remove it and place it on the apparatus. Lower the needle to touch the geopolymer slurry surface, allow it to sink vertically for 30 s under its own weight, and record the depth. If the needle is $4 \text{ mm} \pm 1 \text{ mm}$ from the bottom plate, the geopolymer has reached initial set. The initial setting time is the time from activator addition to this point (in min).

(2) Determination of final setting time

After determining the initial setting time, rotate the specimen and place it in the curing chamber with the larger end up. Replace the final setting needle. Measure every 10 min as the geopolymer nears final set. Final set is reached when the needle penetrates no more than 0.5 mm. The final setting time is the period from alkaline activator addition to final set (in min).

2.3.2. Compressive Strength and Flexural Strength

The flexural strength and compressive strength of geopolymer paste were determined by the cement mortar strength test method. The prepared polymer paste was poured into a 40 mm × 40 mm × 160 mm mold, with 3 specimens in each group, as shown in Figure 3. The mold was vibrated on the vibrating table for 30 s to remove air bubbles. We placed a layer of plastic film on the surface of the specimen to prevent water loss during the curing process. After 24 h, the specimen was removed from the mold and transferred to a standard curing box (YH-60B, Cangzhou Yixuan Testing Instrument Co., Ltd., Cangzhou, China) for curing (the curing conditions are a temperature of 20 ± 1 °C and a relative humidity greater than 90%). After reaching the specified age, the flexural strength (using three-point bending) and compressive strength were measured, as shown in Figure 3.

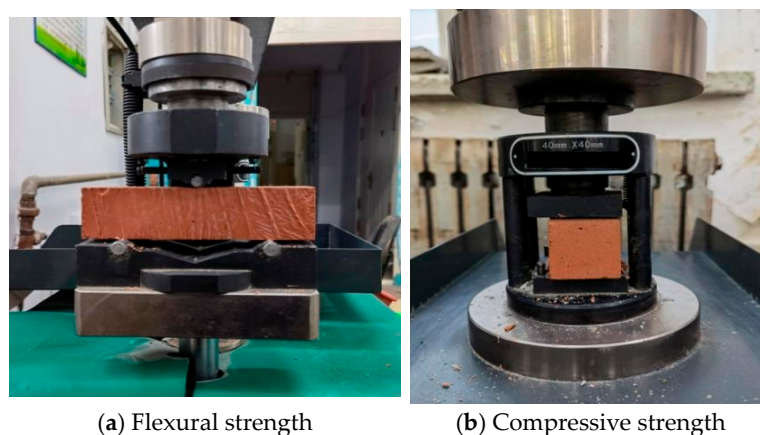


Figure 3. Strength test of geopolymer slurry and mortar.

2.3.3. Microstructure Characterization

(1) Phase analysis

The mineral composition of the raw materials and the geopolymer paste was analyzed by X-ray diffraction (XRD). The working principle is that the energy ϵ of the particle flow and the wavelength λ , frequency h , and speed c of the X-ray photons satisfy the relationship $\epsilon = hc/\lambda$. During the propagation of photons in the sample, when the optical path difference is an integer multiple of the wavelength, superposition occurs, and the diffraction condition of $2d\sin\theta = n\lambda$ is satisfied. Therefore, only the 2θ angle of the mineral phase needs to be measured, and is then compared with the standard card to determine the mineral phase composition. This paper uses the XRD-6100 type X-ray diffraction instrument produced by Shimadzu Corporation (Kyoto, Japan). Its working conditions are as follows: maximum output power, 3 kW; maximum current, 80 mA; maximum voltage, 60 kV; scanning mode is either continuous scanning or step scanning; and the 2θ angle working range is -180° to 180° .

(2) Molecular structure analysis

The molecular structure of the ground polymer paste was analyzed by Fourier transform infrared spectroscopy (Anton Paar Group Corporation, Chicago, IL, USA). The ground samples were mixed with potassium iodide to form thin slices with a thickness of 1 mm and a diameter of 10 mm, and then tested. This study used the Nicolet 50 Fourier transform infrared spectrometer produced by Thermo Fisher Scientific China Co., Ltd. (Shanghai, China), with a resolution of 0.09 cm^{-1} , wave number accuracy of 0.005 cm^{-1} , full spectral linear accuracy better than 0.07%, spectral range of $350\text{--}7800\text{ cm}^{-1}$, and stability with a rapid scanning performance of more than 60 spectra per second.

(3) Microanalysis

The morphological characteristics of the geopolymer paste were characterized by field-emission scanning electron microscopy analysis, and the reaction mechanism of geopolymer was studied. A small piece of sample with a relatively smooth surface was taken, dust was removed, and the sample was then fixed on the sample stage with conductive glue. After spraying a gold conductive layer on the surface, the test was conducted. This study used the JSM-7500F-type variable vacuum scanning electron microscope produced by JEOL Corporation (Tokyo, Japan), 1.5–25 mm (WD) and acceleration voltage range of 0.1 kV to 30 kV.

3. Results and Discussion

3.1. Setting Time

The setting time of geopolymer must meet the construction requirements. If the setting time is too short, it will prevent construction; if it is too long, it will increase the construction period and raise the cost. Geopolymer, a new type of chemical cementitious material, has its setting time primarily affected by the modulus of the alkali activator, the equivalent of Na_2O , temperature, humidity, and mineral admixtures such as slag. This experiment was conducted at an environmental temperature of $20 \pm 2^\circ\text{C}$ and a relative humidity greater than 55%. The specific test results are shown in Figure 4.

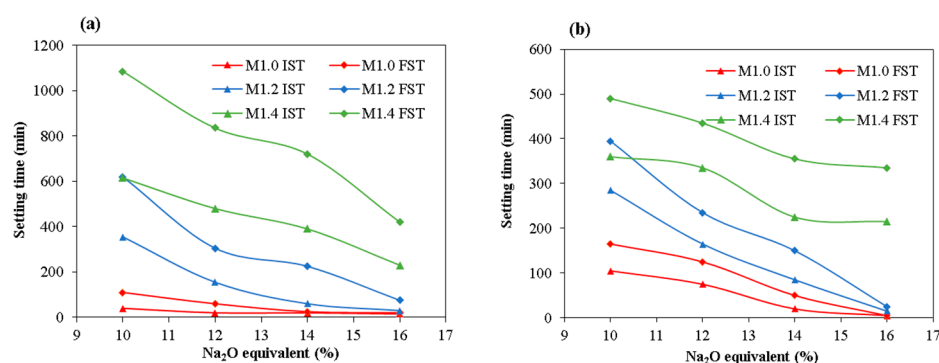


Figure 4. The influence of alkali activator modulus and Na_2O equivalent on the setting time of geopolymers: (a) $\text{P}_{100}\text{F}_0\text{S}_0\text{M}_x\text{N}_y$ and (b) $\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_x\text{N}_y$. (M1.0 denotes an activator modulus of 1.0; IST represents the initial setting time, and FST represents the final setting time).

Figure 4 demonstrates that within the modulus range of 1.0 to 1.4 for the alkali activator, the setting time exhibits a consistent increasing trend with higher modulus values, a phenomenon particularly pronounced when the Na_2O equivalent concentration is between 10% and 12%. This behavior is directly linked to the role of NaOH in modulating the activator's modulus. As the modulus increases, the amount of NaOH decreases, thereby reducing the overall alkaline activity and weakening the solution's alkalinity. This reduction diminishes the effectiveness of OH^- ions in breaking the Si-O, Al-O, and Ca-O bonds present in metakaolin, fly ash, and slag. As a consequence, the hydration and dissolution rates of silicon, aluminum, and calcium species are significantly slowed, limiting the release of silicate and aluminate ions into the geopolymer slurry. The resulting lower ion concentration fails to provide the adequate reactive precursors necessary to sustain rapid geopolymerization, thereby decelerating the overall reaction kinetics and extending the setting time.

When the modulus of the alkali activator remains unchanged, within the range of 10% to 16% of the Na_2O equivalent, an increase in the Na_2O equivalent leads to a shortening of the setting time. The rate of shortening is the greatest within the range of 10% to 12%. The reason for this is that under the condition of a constant alkali activator modulus, an

increase in the Na_2O equivalent is equivalent to an increase in the amount of the alkali activator, thereby increasing the content of SiO_2 and OH^- . This enhances the alkalinity of the alkali activator, strengthens the interaction of OH^- with Si-O, Al-O, and Ca-O bonds in metakaolin, fly ash, and slag, increases the hydration rate of the silicon–aluminum–calcium atoms, accelerates the dissolution rate, and leads to an increase in the concentration of silicate and aluminate ions in the geopolymer slurry, providing sufficient precursors for the entire geopolymer reaction, accelerating the reaction speed, and shortening the setting time. At the same time, when the alkaline level meets the requirements, the increase in SiO_2 content during the polymerization process will provide more precursors, thereby accelerating the polymerization reaction of the geopolymer.

The incorporation of fly ash significantly prolongs the setting time of metakaolin-based polymer cementitious materials due to its pronounced retarding effect. This retardation is attributed to the reduction in alkalinity of the alkali activator caused by fly ash, which slows down the polymerization reaction. In contrast, calcium-containing components in slag effectively accelerate the setting process, thereby shortening the setting time. Under strongly alkaline conditions, an increase in Ca^{2+} content promotes the rapid formation and crystallization of $\text{Ca}(\text{OH})_2$. The resulting $\text{Ca}(\text{OH})_2$ crystals act as nucleation sites that facilitate the generation of C-A-S-H gel, further enhancing early solidification. However, when both fly ash and slag are added to metakaolin-based systems, the overall availability of Ca^{2+} may be reduced to some extent, thereby delaying the formation of C-A-S-H gel. In practical applications, the setting time of metakaolin-based polymer pastes can be tailored to meet specific engineering requirements through the optimization of mixture proportions involving fly ash and slag.

3.2. Compressive Strength and Flexural Strength

The flexural and compressive strength specimens of the geopolymer paste were prepared based on the results of the setting time test. Their compressive and flexural strengths were tested at 3, 7, 14, and 28 days, respectively. The strength change patterns were analyzed, and then the influence of the modulus of the alkali activator and the equivalent of Na_2O on the mechanical properties of the geopolymer under different slag contents was studied. The specific test results are shown in Figures 5 and 6.

As shown in Figures 5a–c and 6a–c, the flexural and compressive strengths of high-calcium metakaolin-based geopolymers increase with curing age. The strength develops rapidly within the first 14 days, after which the rate of increase slows and the strength stabilizes between 14 and 28 days. Compared to ordinary Portland cement, the flexural strength of these geopolymers is relatively lower. An increase in the modulus of the alkali activator and the Na_2O equivalent leads to enhanced flexural and compressive strengths, which is closely related to the $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ molar ratio in the geopolymer system. During geopolymerization, dissolved silica in the alkaline solution promotes the depolymerization of Si-O-T bonds on the surface of solid particles. When the $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ ratio is below the threshold required for the condensation of $\text{Al}(\text{OH})_4^-$, silicate and aluminate species preferentially undergo cross-condensation, forming predominantly low-polymerization-degree aluminosilicates with a relatively limited structural integrity. As the alkali activator modulus increases, so does the $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ ratio, resulting in a higher Si/Al ratio in the reaction system. This promotes initial self-condensation of silicate species into oligomers, which subsequently react with $\text{Al}(\text{OH})_4^-$ to form more highly polymerized aluminosilicate networks—structures that are favorable for geopolymer framework development. However, if the $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ ratio exceeds the optimal range for geopolymerization, an excessive silicate concentration may lead to the formation of cyclic silicate species during condensation. This hinders the polymerization between $\text{Al}(\text{OH})_4^-$ and $\text{Si}(\text{OH})_4$.

monomers or linear SiO_3^{2-} anions. Furthermore, unreacted free SiO_2 remains in the matrix as amorphous SiO_3^{2-} , contributing to a less cohesive and lower-strength hardened product, thereby reducing the overall mechanical performance of the geopolymer.

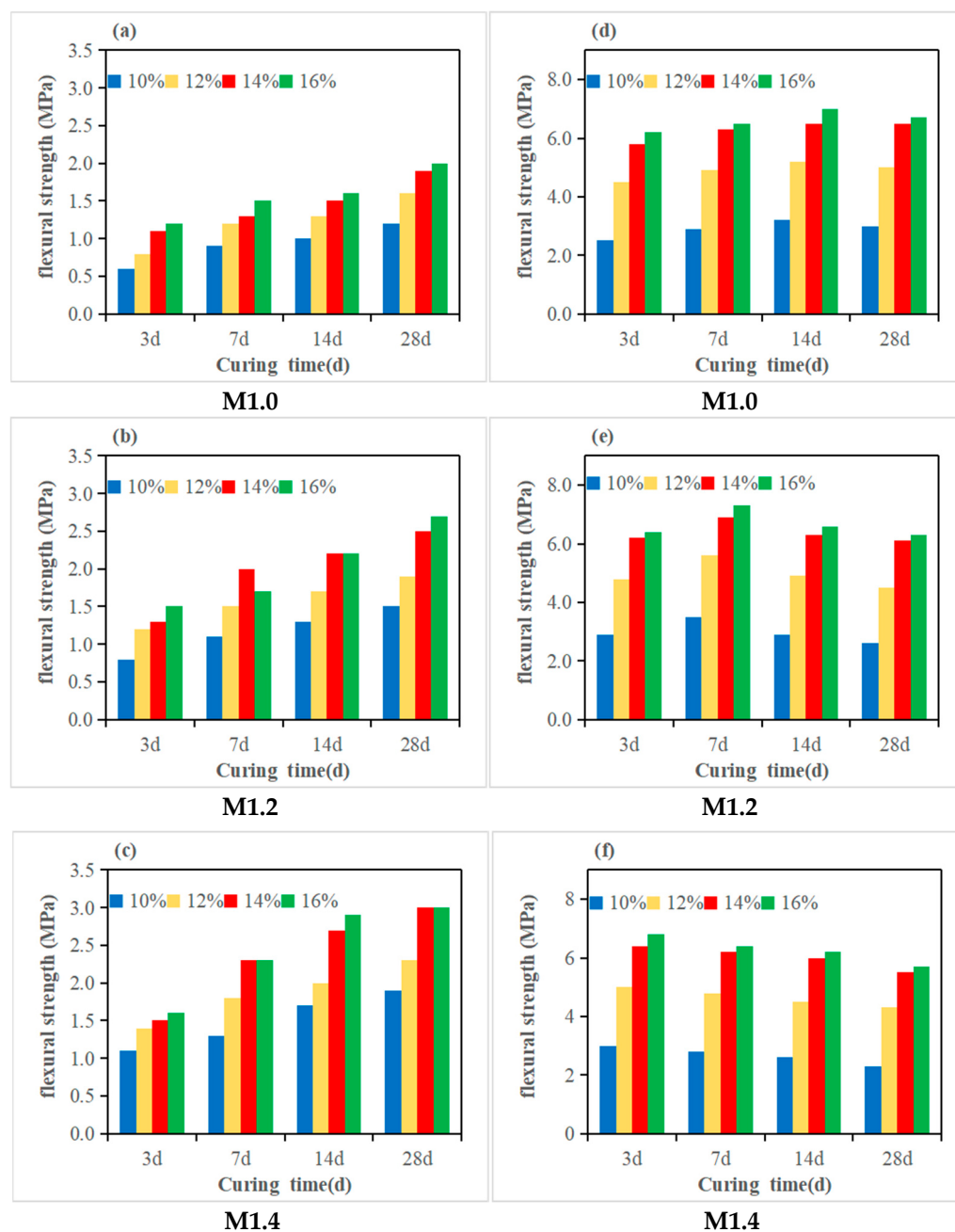


Figure 5. The impact of alkali activator modulus and Na_2O equivalent on the flexural strength of geopolymers: (a–c) $\text{P}_{100}\text{F}_0\text{S}_0\text{M}_x\text{N}_y$ and (d–f) $\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_x\text{N}_y$.

The Na_2O equivalent is also an important factor influencing the geopolymer reaction. When the Na_2O equivalent in the geopolymer is low, its flexural and compressive strengths increase with the increase in the Na_2O equivalent. Beyond the critical value, they will decrease as the Na_2O equivalent increases. The geopolymer reaction is composed of a series of depolymerization and polycondensation reactions. The initial degree of depolymerization directly affects the subsequent polycondensation reaction. The degree of depolymerization of silicate–aluminate increases with the increase in the concentration of $(\text{OH})^-$ ions in the system, generating more siloxane and aloxane monomers to participate in the subsequent polycondensation reaction, promoting the growth of geopolymer strength. When the Na_2O

equivalent exceeds the critical value and continues to increase, excessive Na_2O will cause unevenness in the low-polymer products, promoting the premature precipitation of the geopolymer gel and encapsulating the unreacted metakaolin particles, thereby inhibiting the depolymerization reaction and reducing the strength of the geopolymer. An excessive alkali concentration will cause Na^+ adsorbed on the solid particles of metakaolin to react with $\text{Al}(\text{OH})_4^-$ and $\text{Si}(\text{OH})_4$, reducing the adhesion between the solid insoluble particles and the silicate–aluminate gel in the system. At the same time, the excessive Na^+ adsorbed on the surface of the solid, insoluble particles will also react with CO_2 in the air to undergo carbonation, which hinders the growth of geopolymer strength.

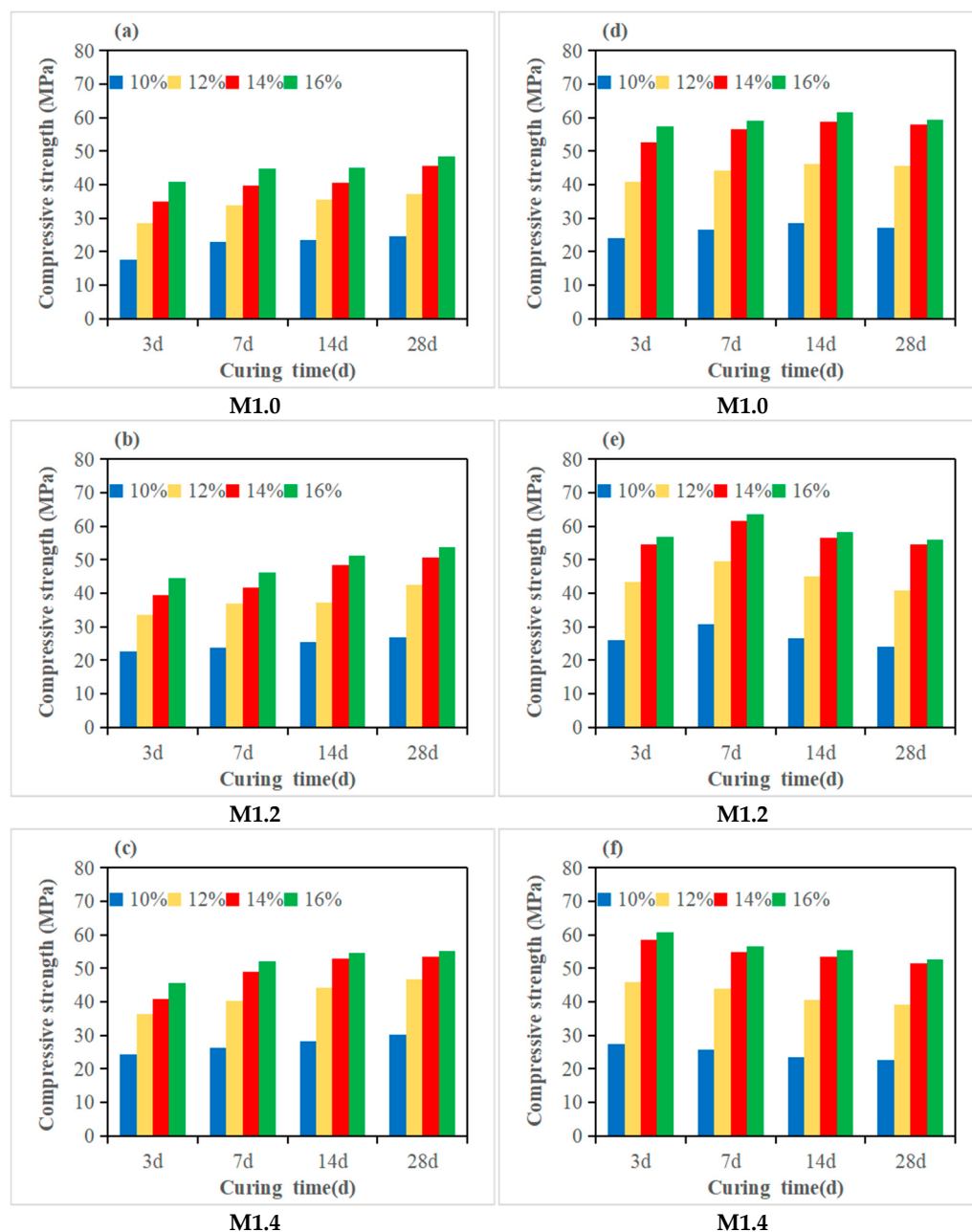


Figure 6. The impact of alkali activator modulus and Na_2O equivalent on the compressive strength of geopolymers: (a–c) $\text{P}_{100}\text{F}_0\text{S}_0\text{M}_x\text{N}_y$ and (d–f) $\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_x\text{N}_y$.

The flexural and compressive strengths of the metakaolin geopolymer in this paper continuously increase within the range of 2.47 to 2.97 $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ and 10% to 16%

Na₂O equivalent, indicating that neither reach the critical value. The maximum strength mix ratio is P100F0S0M1.4N16.

Figures 5d–f and 6d–f show that the flexural and compressive strengths of fly ash and slag–metakaolin geopolymers increase with the increase in age. The flexural and compressive strengths of the fly ash and slag–metakaolin geopolymers increase rapidly from 0 to 7 days, and then tend to stabilize from 7 to 28 days. At 28 days, they reach relatively high flexural and compressive strengths. The CaO content in slag is relatively high. In a strong alkaline environment, the Ca–O bonds are more likely to be rapidly dissociated and dissolved by (OH)[−] than Al–O bonds and Si–O bonds. In the early stage of the reaction, Ca²⁺ can rapidly react to form hydrated calcium silicate (C–S–H) and hydrated silicate aluminum calcium (C–A–S–H) gels, accelerating the polymerization reaction and increasing the early strength of the geopolymers. At the same time, the two gel products generated can fill the voids between unreacted particles, thereby improving the compactness of the geopolymers and enhancing their structural strength. Additionally, the water in the C–S–H and C–A–S–H gels enters the structure of the geopolymers, reducing the evaporable water content and effectively improving the pore structure distribution of the geopolymers, thereby enhancing the overall durability of the geopolymer concrete.

Furthermore, the volcanic ash reaction mechanism of fly ash in ordinary Portland cement achieves the same effect as the polymerization reactions of the fly ash, slag–metakaolin composite. When fly ash is in a strongly alkaline environment and under the action of polar (OH)[−], the Al–O bonds and Si–O bonds break, reacting with Ca²⁺ in the system to form hydrated silicacalcium (C–S–H) and hydrated silicotungstosilicacalcium (C–A–S–H) gels, thereby enhancing the strength of the geopolymers; at the initial stage of the development of the geopolymer strength, fly ash has a micro-aggregate filling effect, playing a physical filling role, which can reduce the proportion of harmful pores in the internal structure of the slurry and result in a uniform and dense slurry.

When the modulus of the fly ash and slag–metakaolin polymer is fixed at 1.0, the strength value increases initially and then decreases as the Na₂O content increases. When the equivalent Na₂O content is 14%, the flexural and compressive strengths reach their maximum values of 7.0 MPa and 61.5 MPa, respectively. As the modulus is fixed at 1.2, the strength value increases initially and then decreases as the Na₂O content increases. When the equivalent Na₂O content is 12%, the flexural and compressive strengths reach their maximum values of 7.3 MPa and 63.5 MPa, respectively. When the modulus is fixed at 1.4, the strength decreases as the Na₂O content increases. When the equivalent Na₂O content reaches 10%, the flexural and compressive strengths attain their maximum values of 6.8 MPa and 60.8 MPa, respectively. The $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ of the three cases is 3.26, 3.28, and 3.28, respectively, indicating that 3.28 reaches the optimal molar ratio of (SiO₂)/(Al₂O₃) for the polymer. When $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ is less than 3.28, as the (SiO₂)/(Al₂O₃) molar ratio increases, the low polymeric silicaluminate salts gradually transform into polymeric silicaluminate salts, and the strength continues to increase; when $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ is greater than 3.28, as the SiO₂/Al₂O₃ molar ratio increases, the amount of free SiO₂ in the amorphous SiO₃^{2−} form that exists in the polymer system without reacting increases, and the strength continues to decrease.

Determining the optimal SiO₂/Al₂O₃ molar ratio for fly ash and slag–metakaolin-based geopolymer systems can significantly simplify the mix design process. The formulation with the highest compressive strength is identified as P₆₀F₂₀S₂₀M_{1.2}N₁₂.

3.3. Characterization of Reaction Products

3.3.1. XRD Analysis

The 28-day XRD patterns of silicon–aluminaceous raw materials such as metakaolin (RAW-P), slag (RAW-S), fly ash (RAW-F), and geopolymers ($P_{100}F_0S_0M_{1.4}N_{16}$, $P_{60}F_{20}S_{20}M_{1.2}N_{12}$) are shown in Figure 7.

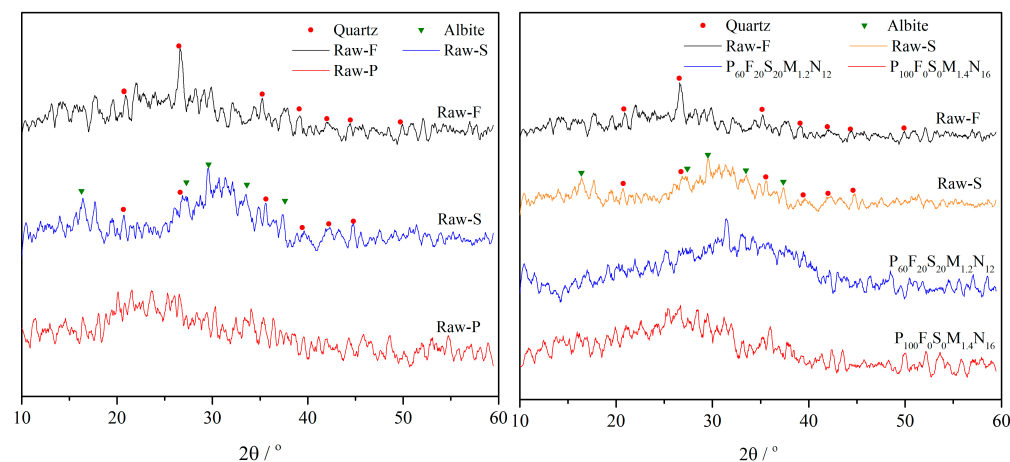


Figure 7. XRD patterns of geopolymer, metakaolin and slag.

High alumina and slag mainly consist of amorphous phases. The high alumina contains only a weak quartz (Quartz) characteristic peak, while the slag also contains quartz and albite ($NaAlSi_3O_8$) phases. The crystallinity of fly ash increases, and obvious quartz components can be observed. After the raw materials with different compositions undergo polymerization reactions under the action of alkali activators, the diffraction angle 2θ of the geopolymers appears broader, with amorphous diffuse diffraction peaks within the range of 10 to 45 degrees, moving to higher angles compared to the raw materials, and new phase diffraction peaks can be clearly observed. This indicates that the high-alumina raw material participates in the polymerization reaction and dissolves into the new phase, resulting in the formation of new substances. Through the comparison of diffraction peaks, characteristic peaks of quartz or albite can still be observed in the geopolymers, but their intensities have significantly weakened. Some samples cannot even be observed. This indicates that in the presence of alkali activators, the slag and fly ash participate in the polymerization reaction and are consumed, while the quartz and albite components they contain transform, with the intensity of the characteristic peaks weakening.

Taking the best mechanical performance among the two mixing ratios of silicate raw materials, such as fly ash and slag–metakaolin composite, as an example, the influence of modulus and Na_2O equivalent on the mechanical properties of the geopolymer was analyzed. With the modulus fixed at 1.2, the XRD spectra of different Na_2O equivalent geopolymers are shown in Figure 8. It can be seen that the greater the Na_2O equivalent, the wider the amorphous dispersion peak becomes, indicating a higher proportion of amorphous gel component. When the Na_2O equivalent is 10%, the amorphous peak is significantly shifted to a lower angle, indicating that more metakaolin has not yet reacted completely. When the Na_2O equivalent reaches 12%, the amorphous component is the largest, and there is almost no crystalline component. Such a composition may make its strength higher than that of other samples, because the strength of the geopolymer is determined by the gelation effect between the newly formed silicate–aluminate gel bodies in the reaction system. The larger the proportion of the amorphous gel phase, the better the mechanical properties and stability. Conversely, the higher the crystallization degree, the lower the chemical bond strength, and the lower the product strength. As the Na_2O

equivalent increased to 14% and 16%, the XRD spectra indicated a higher amorphous content, although the crystalline characteristics remained discernible. This compositional profile may potentially compromise the mechanical strength of the sample.

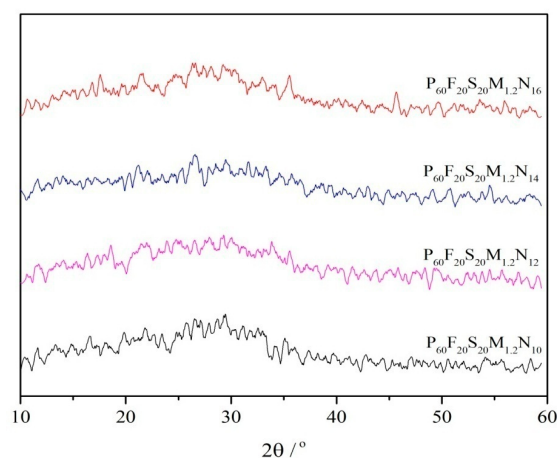


Figure 8. XRD patterns of geopolymers with varying Na_2O equivalents at a fixed modulus of 1.2.

The XRD patterns of geopolymer samples with varying moduli and a fixed Na_2O equivalent of 12% are presented in Figure 9. As shown in the analysis, compared to the characteristic peaks of quartz and albite observed in the raw slag material, the amorphous hump is the broadest at a modulus of 1.2 and shifts furthest toward higher diffraction angles. Furthermore, nearly no distinct quartz or albite peaks are detectable, suggesting that the polymerization reaction in this sample is the most extensive, with the highest content of amorphous components and, consequently, the greatest mechanical strength.

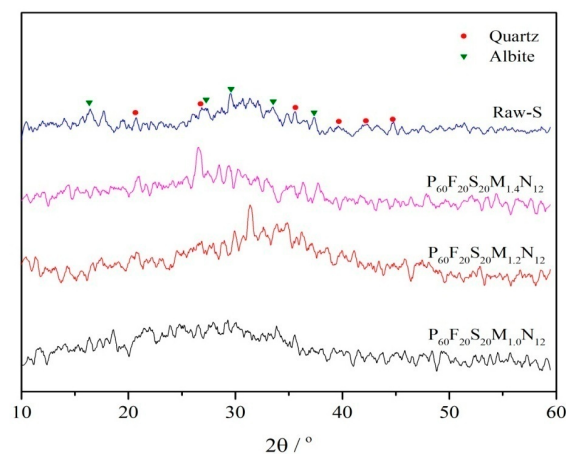


Figure 9. XRD patterns of geopolymer with different modulus under Na_2O equivalents 12%.

3.3.2. Infrared Spectroscopic Analysis

The infrared spectra of 28-day-aged raw metakaolin (Raw-P), raw fly ash (Raw-F), raw slag (Raw-S), and two geological polymers, $\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.4}\text{N}_{16}$ and $\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.2}\text{N}_{12}$, are shown in Figure 10. The infrared vibration spectral bands of functional groups are presented in Table 6.

Table 6. Infrared vibration bands of functional group characteristics.

Wave Number/ cm^{-1}	Key Type	References
796, 778, 692, 688	Quartz	[29]
1091, 1078	Vibration Si-O-Si	[30]

Table 6. Cont.

Wave Number/cm ⁻¹	Key Type	References
1640, 1632	Bending vibration H-O-H	[31]
1453, 1385	Asymmetric stretching O-C-O	[32,33]
560	Stretching vibration Al-O	[34]
580	Asymmetric stretching vibration T-O	[34]
1024	Asymmetric stretching vibration Si-O-T ^a	[35]
460	Bending vibration T-O	[35]

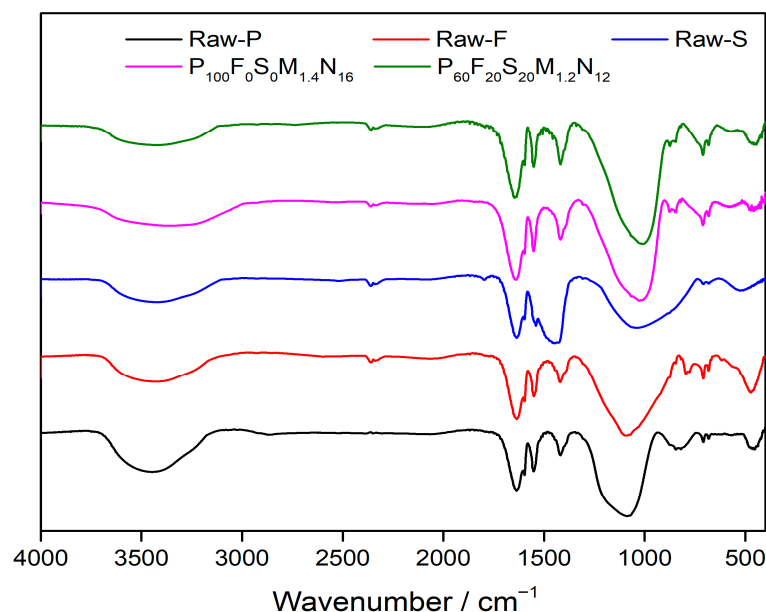
Note: T^a = Al, Si.

Figure 10. FTIR patterns of geopolymers, metakaolin, fly ash, and slag.

According to the data presented in Table 6 and the analysis shown in Figure 10, the three raw materials—high-calcium metakaolin, fly ash, and slag—exhibit distinct absorption peaks within the range of 1064–1073 cm⁻¹. These peaks correspond to the stretching vibrations of Si-O-Si bonds, which are consistent with the elemental compositions of the raw materials. By comparing two different geopolymer formulations, it can be observed that this characteristic peak undergoes a shift of approximately 60 cm⁻¹ toward lower wavenumbers (red shift). The maximum absorption peaks for P₁₀₀F₀S₀M_{1.4}N₁₆ and P₆₀F₂₀S₂₀M_{1.2}N₁₂ are located at 1008 cm⁻¹ and 1015 cm⁻¹, respectively. This shift is attributed to partial substitution of Al for Si within the Si-O-Si functional group, leading to the formation of Si-O-Al bonds. This substitution reduces the vibrational bond energy, thereby causing the absorption peak to move to a lower frequency, resulting in a red shift. Such spectral changes indicate that the raw materials have undergone chemical reaction under alkali activation, leading to the formation of a silicate gel network. Additionally, the absorption peak at 828 cm⁻¹ in high-calcium metakaolin corresponds to the Al-O vibration of six-coordinate aluminum. After geopolymerization, this peak diminishes or disappears, and a new absorption peak emerges at approximately 710 cm⁻¹, which is associated with the vibration of four-coordinate [AlO₄]⁵⁻ tetrahedra within the silicate gel structure. The transformation of aluminum from six- to four-coordination further confirms that the geopolymerization reaction has taken place.

Taking the best mechanical performance among the two silicon–aluminum raw material blending ratios as an example, using the fly ash, slag–metakaolin composite as the material, the influence of modulus and Na₂O equivalent on the mechanical properties of the geopolymer was analyzed. With modulus fixed at 1.2, the infrared spectra and

characteristic peak intensities of different Na_2O equivalent geopolymers are shown in Figures 11 and 12. As illustrated in Figure 11, the FTIR absorption peak data clearly indicate the formation of Si-O-Ta (Ta = Si/Al) characteristic functional groups at approximately 1000 cm^{-1} , suggesting that metakaolin, fly ash, and slag have undergone alkali activation and transformed into geopolymer gels. A comparison of the infrared spectra reveals that the characteristic vibration peak of HCO_3^- appears at 1418 cm^{-1} , and this peak becomes increasingly pronounced with higher Na_2O equivalents. This phenomenon is attributed to the enhanced absorption of atmospheric CO_2 by the excess alkali during the geopolymerization process. These observations confirm that the added alkali activator actively participates in the polymerization reaction.

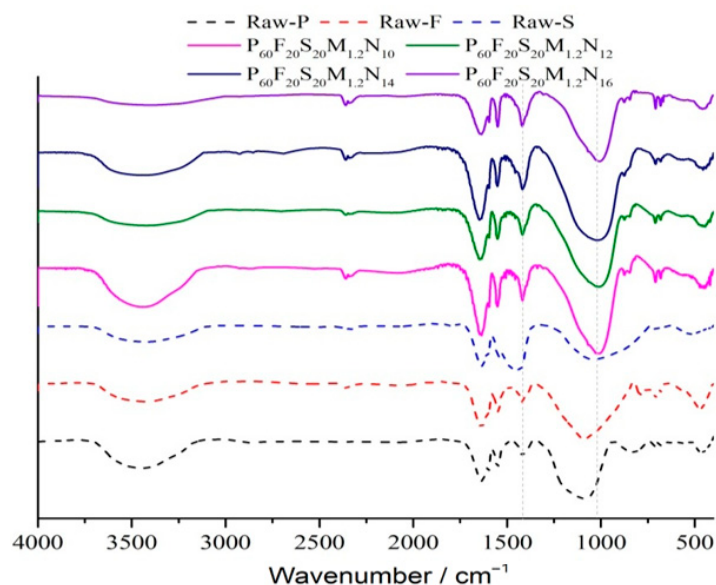


Figure 11. FTIR patterns of geopolymer with different Na_2O equivalents under modulus 1.2.

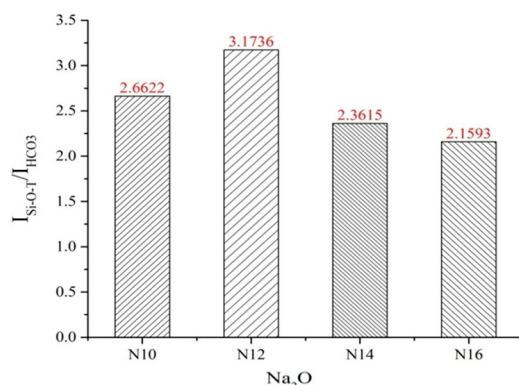


Figure 12. Correlation between characteristic peak intensity ratio and Na_2O equivalent.

Based on the aforementioned analysis, the absorption peak at approximately 1000 cm^{-1} corresponding to the Si-O-Ta functional group can serve as an indicator of the degree of polymerization of the raw materials. Meanwhile, the absorption peak at 1418 cm^{-1} reflects the involvement of NaOH in the polymerization reaction. Although the intensity of infrared spectra cannot be precisely quantified, comparing the relative peak intensities among different samples can provide a qualitative assessment to some extent. Therefore, the $I_{\text{HCO}_3^-} / I_{\text{Si-O-Ta}}$ ratios of four samples with varying Na_2O equivalents were compared, as illustrated in Figure 12. The analysis reveals that when the Na_2O equivalent is 12%, the relative Si-O-Ta absorption peak is the most intense, indicating the highest

degree of geopolymerization. At this alkali dosage, the system demonstrates the strongest alkali activation capability and achieves the maximum mechanical strength.

The infrared spectra of geopolymers with varying moduli and a fixed Na_2O equivalent of 12% are presented in Figure 13. It can be observed that all three samples exhibit distinct absorption peaks within the range of $1008\text{--}1200\text{ cm}^{-1}$. Compared to the raw materials, a red shift of approximately 60 cm^{-1} is evident. This phenomenon, as previously discussed, is attributed to the occurrence of geopolymerization, during which some Si atoms in the Si-O-Si functional groups are partially substituted by Al, forming Si-O-Al bonds. Consequently, the vibrational bond energy decreases, leading to a shift in the absorption peak to lower wavenumbers, which serves as an indicator of the polymerization reaction. The absorption peaks in the range of $650\text{--}750\text{ cm}^{-1}$ correspond to the transformation of six-coordinated Al in the raw materials into four-coordinated $[\text{AlO}_4]^{5-}$ tetrahedra within the silicate gel structure. This transformation confirms the microstructural evolution of the raw material composition. Upon close examination of the spectra of the three samples, it is evident that the infrared absorption peaks within the range of $650\text{--}750\text{ cm}^{-1}$ gradually weaken as the modulus increases. This behavior can be explained as follows: when the modulus is low, the SiO_4 content in the system is limited, and four-coordinated AlO_4 enters the SiO_4 network but fails to reach structural saturation. As the modulus increases, the SiO_4 content rises. When the modulus reaches 1.2, AlO_4 integrates into the SiO_4 network and approaches equilibrium, indicating a more complete reaction. As the modulus continues to increase beyond this point, an excess of SiO_4 broadens the Si-O-T absorption peak and causes it to gradually weaken.

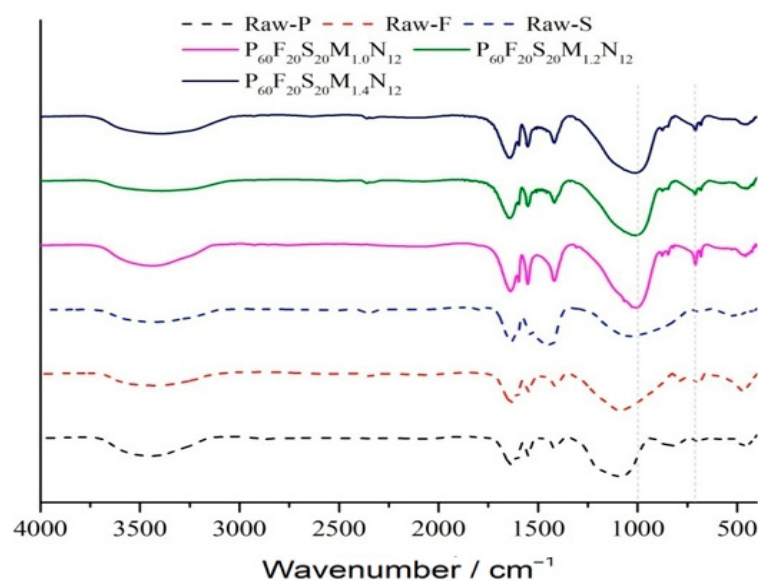


Figure 13. FTIR patterns of geopolymer with different modulus under Na_2O equivalents 12%.

3.3.3. SEM Analysis

The microscopic morphologies of the geoaggregates $\text{P}_{100}\text{F}_0\text{S}_0\text{M}_{1.4}\text{N}_{16}$ and $\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.2}\text{N}_{12}$ were analyzed by scanning electron microscopy (SEM), as shown in Figure 14. Taking $\text{P}_{60}\text{F}_{20}\text{S}_{20}\text{M}_{1.2}$ as an example, under the premise of a fixed modulus, the microscopic morphologies of different Na_2O equivalents were analyzed, as shown in Figure 15.

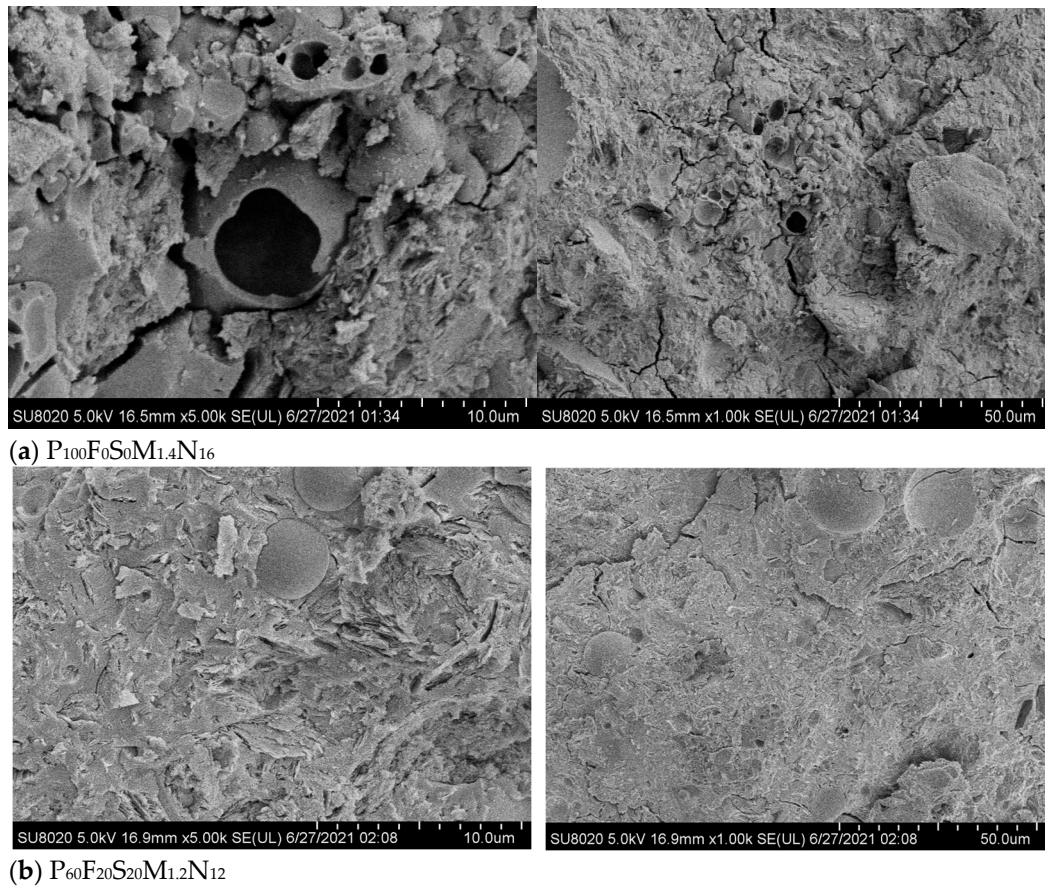


Figure 14. SEM patterns of geopolymer.

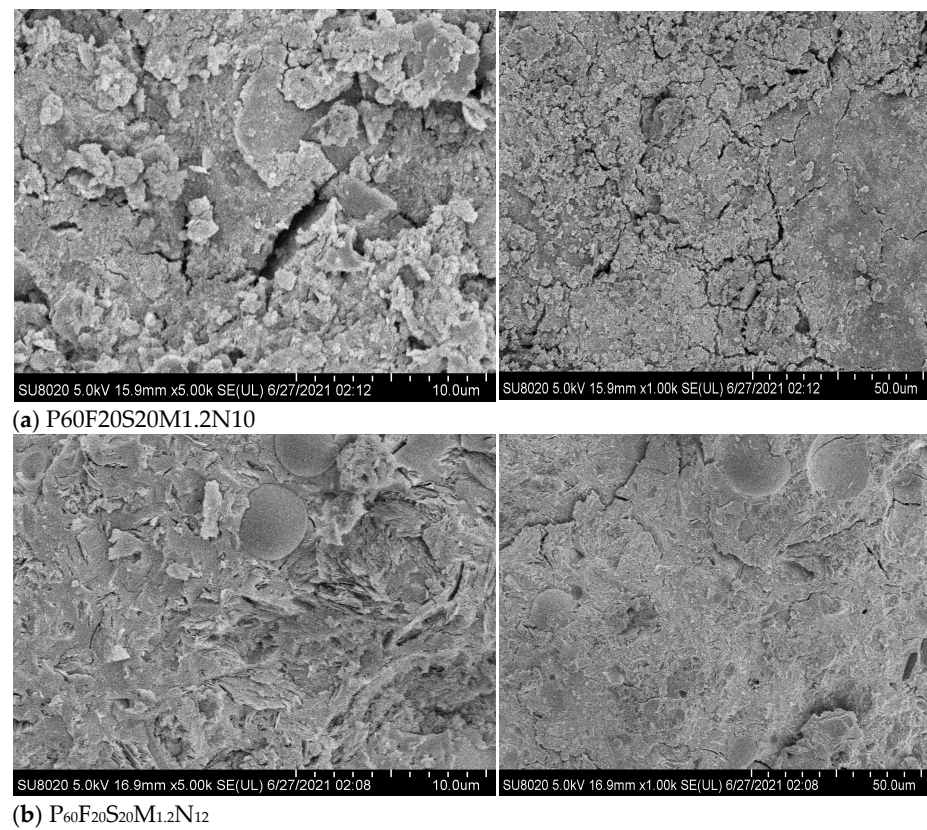


Figure 15. Cont.

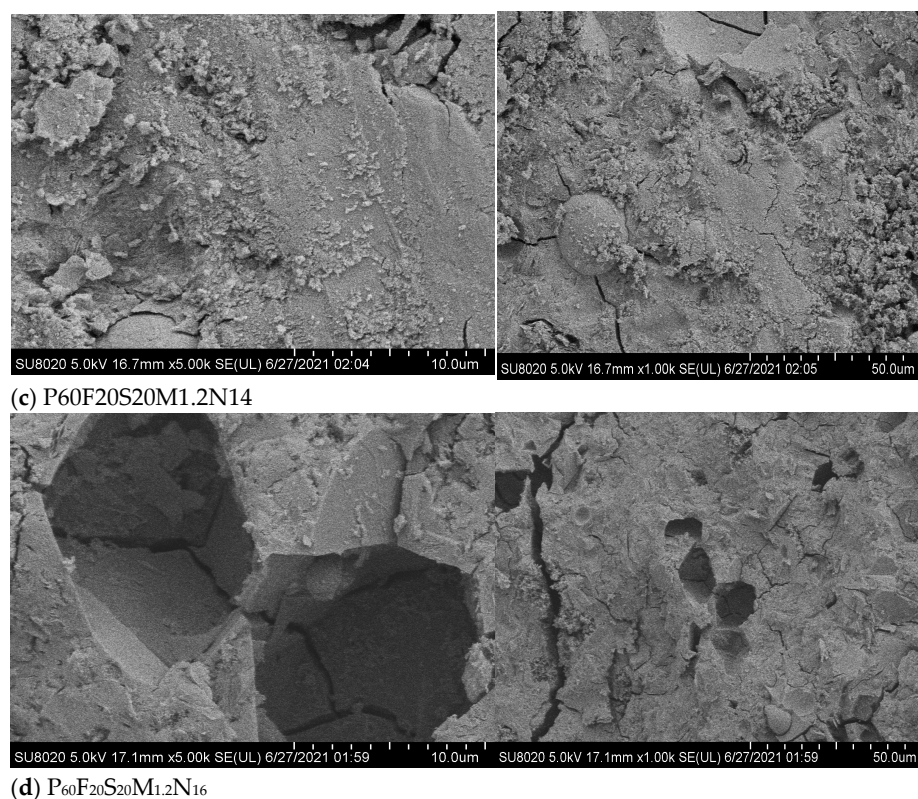


Figure 15. SEM patterns of $P_{60}F_{20}S_{20}M_{1.2}N_{14}$ SEM geopolymer.

As shown in the SEM image of the geopolymer presented in Figure 14a, the $P_{100}F_0S_0M_{1.4}N_{16}$ sample exhibits a loose slurry structure characterized by numerous pores and microcracks. These structural features contribute to the relatively low mechanical strength of the geopolymer. In contrast, the SEM image in Figure 14b demonstrates that the calcium silicate (C-S-H) and calcium aluminosilicate (C-A-S-H) gels formed during the geopolymerization process are capable of filling the interparticle voids, unreacted regions, and microcracks at various reaction stages. This results in a more compact and densely structured geopolymer matrix, thereby enhancing its overall mechanical properties.

From the SEM image of the geopolymers in Figure 15, it can be clearly seen that the compactness of the geopolymers' particle structure increases initially and then decreases as the Na_2O equivalent increases. The reason for this is that when the Na_2O equivalent exceeds the critical value, the geopolymer gel will precipitate prematurely, encapsulating the unreacted fly ash and metakaolin, thereby inhibiting the progress of the depolymerization reaction. The prematurely precipitated gel cannot promptly fill the microcracks and interparticle voids that have not yet reacted in the later reaction. As the Na_2O concentration continues to increase, the cracks and pores expand continuously.

4. Conclusions

This study utilized high-purity metakaolin as the primary silica–alumina source and employed a mixture of sodium silicate and NaOH as the alkali activator to synthesize geopolymer. The mechanical performance of the geopolymer was enhanced through the incorporation of fly ash and slag. Single-factor experimental designs were conducted to investigate the effects of sodium silicate modulus, Na_2O equivalent, fly ash content, and slag content on the setting time and compressive strength of the geopolymer paste. XRD, FTIR, and SEM analyses were employed to characterize the phase composition, molecular structure, and microstructural morphology of the geopolymer, thereby elucidating the micro-mechanism underlying strength development. These findings provide fundamental

data for the formulation of geopolymer mortar and concrete. The main research findings are summarized as follows:

- (1) The setting time of the alkali activator increases with an increasing modulus within the range of 1.0 to 1.4. Under constant modulus conditions, the setting time decreases as the Na₂O equivalent increases from 10% to 16%. The incorporation of fly ash and slag significantly reduces the setting time of the geopolymer system.
- (2) The molar ratio $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ is a critical factor influencing geopolymer strength. Under fixed-modulus conditions, the effect of Na₂O on strength becomes particularly pronounced. For high-metakaolin-based geopolymers, both flexural and compressive strengths increase continuously with $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ ratios ranging from 2.47 to 2.97 and Na₂O equivalents ranging from 10% to 16%, indicating that neither parameter has reached its critical threshold. When the $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ ratio of fly ash- and slag-modified metakaolin reaches 3.28, the 28-day flexural and compressive strengths attain maximum values of 7.3 MPa and 63.5 MPa, respectively.
- (3) Based on XRD and FTIR spectral analyses, two optimal geopolymer formulations—P₁₀₀F₀S₀M_{1.4}N₁₆ and P₆₀F₂₀S₂₀M_{1.2}N₁₂—are identified under varying proportions of high-alkali metakaolin, fly ash, and slag. Shifts in the characteristic absorption peaks of metakaolin, fly ash, and slag confirm the occurrence of the geopolymerization reaction and the formation of geopolymer gels. SEM analysis further reveals that the P₆₀F₂₀S₂₀M_{1.2}N₁₂ formulation exhibits the most compact microstructure and superior mechanical properties.
- (4) Using the fly ash and slag–metakaolin geopolymers with the best mechanical performance as a case study, XRD analysis demonstrates that the P₆₀F₂₀S₂₀M_{1.2}N₁₂ geopolymer exhibits minimal characteristic peaks of quartz and albite, indicating a highly complete polymerization reaction. This leads to the formation of a substantial amount of amorphous silicate gel with excellent inter-gel bonding, resulting in optimal mechanical properties. FTIR analysis further confirms that this formulation exhibits the strongest relative Si-O-T absorption peak, the highest degree of geopolymerization, the most effective alkali activation, and, consequently, the greatest mechanical strength.

However, the scope of this study is primarily limited to the mechanical properties and microstructural characteristics of geopolymers. Research on their durability and dry shrinkage behavior remains insufficient. Future work will extend to these aspects, thereby further advancing the application of geopolymers in the construction materials industry and fully demonstrating their significant potential as a novel “green” and environmentally friendly cementitious material.

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Conflicts of Interest: Author Zeming Song was employed by the company Heilongjiang Construction Technology Development Center Co., Ltd. Author Li Wu was employed by the company Heilongjiang Pengcheng Inspection and Testing Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as potential conflicts of interest.

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